2007

# Novel Differential Surface Stress Sensor for Detection of Chemical and Biological Species

Kyungho Kang
*Iowa State University*

Pranav Shrotriya
*Iowa State University*, shrotriy@iastate.edu

Mater. Res. Soc. Symp. Proc. Vol. 1052 © 2008 Materials Research Society 1052-DD05-10

# Novel Differential Surface Stress Sensor for Detection of Chemical and Biological Species

Kyungho Kang, and Pranav Shrotriya
Mechanical Engineering Department, Iowa State University, 2025 Black Engineering Building, Ames, IA, 50011

## ABSTRACT

A miniature sensor consisting of two adjacent micromachined cantilevers (a sensing/reference pair) is developed for detection of chemical and biological species. A novel interferometric technique is utilized to measure the differential bending of sensing cantilever with respect to reference. Presence of species is detected by measuring the differential surface stress associated with adsorption/absorption of chemical species on sensing cantilever. Surface stress associated with formation of alkanethiol self-assembled monolayers (SAMs) on the sensing cantilever is measured to characterize the sensor performance.

## INTRODUCTION

Microcantilever based sensors are increasingly being investigated to detect the presence of chemical and biological species in both gas and liquid environments. Thundat et. al. [1] reported the static deflection of microcantilevers due to changes in relative humidity and thermal heating and thus opened a myriad of possibilities for the use of AFM cantilever deflection technique for chemical and biological sensing. Cantilever based sensors have been successfully demonstrated for DNA sequence recognition and as electrical noses to detect chemical mixtures [2]. In majority of the current state of art sensors, molecule absorption induced surface stress change is inferred from the deflection of a single or multiple laser beams reflected from the sensing surface. A large optical path is required between sensitized surface and position sensitive detectors to achieve high sensitivity in surface stress measurement. As a result, it is difficult to implement the sensing scheme into a single micro-fabricated device. In the current paper, we report a novel differential surface stress sensor that utilizes a single-mode fiber based Mach-Zehnder interferometer for measuring cantilever deflection and consequently, the detection of chemical and biological species. The interferometric technique is amenable to miniaturization and may facilitate the integration of all components of sensors into a single microfabricated chip.

Measurement of surface stress associated with formation of alkanethiol self assembled monolayer (SAM) on a gold surface is utilized to characterize the performance of differential surface stress sensor. Berger et. al. [3] reported the generation of compressive stresses on the order of 0.1-0.5 N/m during the formation of alkanethiol self-assembled monolayer on the cantilever's surface and also reported that the magnitude of surface stress increased linearly with the carbon chain backbone of the monolayer. Since the first report by Berger et. al. [3], SAMs have been used as test system for almost all cantilever based sensing techniques [4-6]. This is because they are relatively easy to prepare, form well-ordered close packed films and offers limitless possibilities of variations in chain length, end group and ligand attachments [7]. One of

the commonly studied SAMs are alkanethiol SAMs ($HS-(CH_2)_{n-1}CH_3$) in which n is the number of carbon atoms in the alkyl chain. Godin et. al. [4] have shown that the kinetics of formation of self-assembled monolayers on gold-coated cantilevers and the resulting structure are dependent on the microstructure of the gold film and also the rate at which the SAM reaches the surface.

## SENSING PRINCIPLE

The differential surface stress sensor consists of two adjacent cantilevers, a sensing/reference pair, where only the sensing surface is activated for adsorption of chemical or biological molecules (Figure 1 A). Absorption/adsorption of analyte species on the sensitized surface is expected to induce differential bending and deflection between the sensing and reference cantilevers. The microcantilevers and a pair of microlens arrays are arranged in the optical arrangement shown schematically in Figure 1B to measure the differential displacement between sensing and reference cantilevers. In this optical configuration, incident laser beam at points A and C always arrives to points B and D, respectively, regardless of their incident angle and differential bending produces a change in path length difference between the beams reflected from the two cantilevers. .

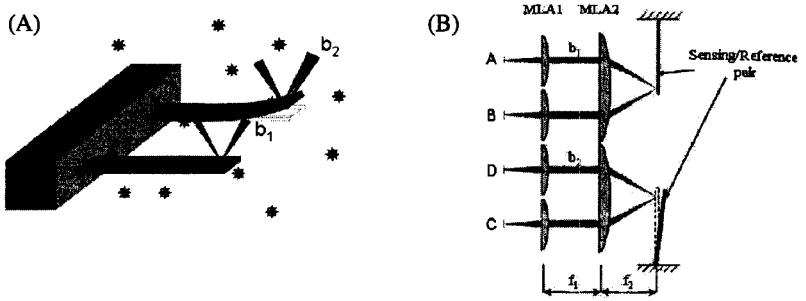


**Figure 1.** Schematic illustration of the sensing principle. (A) Conceptual view of alkanethiol molecule absorption on the gold surface of sensing/reference cantilevers and the consequent differential bending. (B) Principle of differential surface stress measurement.

After reflecting from the sensing and reference surfaces, the two beams accumulate a path length difference, $l$, equal to twice the differential displacement between sensing and reference surface. The beams are interfered to measure the path length difference and differential surface stress ($\Delta\sigma$) between the two cantilevers is determined using Stoney's formula [8].

$$\Delta\sigma = \left(\frac{E}{3(1-\nu)}\right)\left(\frac{t}{L}\right)^2 l$$

where, $E$, is the elastic modulus and $\nu$ is the Poisson's ratio, $L$ is the length and $t$ is thickness of the cantilevers. Measurement of differential surface stress ensures that detected signal is proportional to specific absorption of analyte species on the sensing cantilever and eliminates the influence of environmental disturbances such as nonspecific adsorption, changes in pH, ionic strength, and especially the temperature

## EXPERIMENT

### Differential surface stress sensor realization

An optical circuit shown in Figure 2(A) is utilized for assembling the surface stress sensor. In the system, two adjacent rectangular-tipless AFM cantilevers were used as a sensing/reference pair. A pair of MLAs (microlens arrays) with lens of 240 μm and 900 μm diameters and pitches of 250 μm and 1mm respectively were used to direct the beams towards the sensing/reference pair. Motorized and manual actuators were used to assist in aligning of MLAs with respect to the sensing/reference cantilevers. A bi-directional coupler was applied to split the beam from a 635nm fiber coupled laser source and delivered to MLA1 at 50/50 ratio. Other two reflected beams were interfered using the second bi-directional coupler and intensity of interfered beam was monitored using photodetectors.

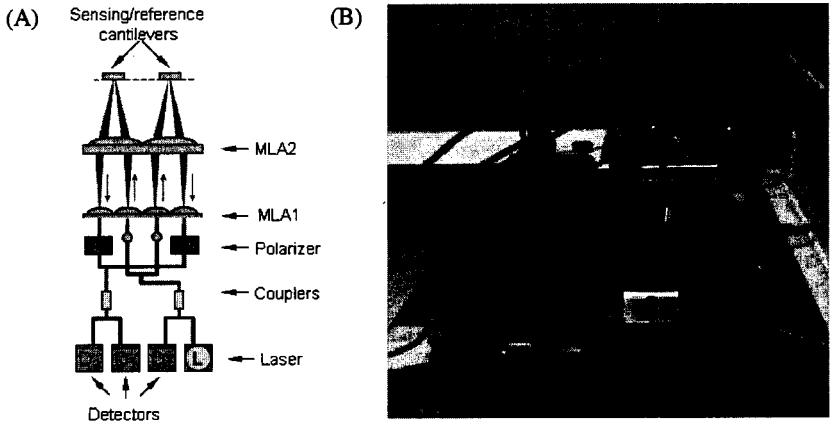


**Figure 2.** Optical circuit of differential surface stress sensor (A) and Photograph of experimental setup (B).

The polarization plane of the reflected beams was matched and common mode rejection was utilized to ensure maximum fringe visibility in the inferred beams. An isolation box covered all fiber couplers as well as sensor components to eliminate acoustic and vibrational noise from the system.

### Cantilever

Silicon cantilevers used in the sensor realization are 480 μm long, 80 μm wide, and 1 μm thick with a top side coating of 5nm titanium and 30nm gold film. (Nanoworld, Switzerland). AFM cantilevers are batch produced with large variation of dimensions and mechanical properties from the manufacture's quote [9, 10]. In order to accurately measure surface stress development, the thickness of each cantilever is calculated based on the experimentally measured spring constant with the material constants [9]. Microstructure and surface roughness of the gold film were determined using contact mode atomic force microscope imaging.

## Experimental procedure

Liquid octanethiol [$CH_3(CH_2)_7SH$] was selected as alkanethiol solution and purchased from Sigma-Aldrich. All the AFM cantilevers were cleaned by immersing for 30 minutes in piranha solution (70% $H_2SO_4$, and 30% $H_2O_2$ by volume) and were then rinsed in deionized water and dried in the gentle N2 flow. Only the reference cantilevers were incubated in pure octanethiol solution for 12 hours to ensure the formation of a self assembled monolayer (SAM) on the gold film. Formation of a stable SAM on the reference cantilever ensures that alkanethiol molecules are only absorbed on the sensing cantilever during subsequent experiments.

Surface stress development associated with alkanethiol SAM formation was measured in three steps. In the first step, reference and sensing cantilever were mounted in the sensor and stability of the interferometer was first checked to ensure that measured signal is not affected by drift and ambient noise. In the second step, 20 mL of pure liquid octanethiol was injected into a beaker placed near the two cantilevers. The vapors of alkanethiol solutions were confined near the cantilevers and interferometer was utilized to measure the deflection of sensing cantilever associated with deposition and formation of alkanethiol SAMs. Intensity of the interfered beams as well as back reflection from the first coupler were monitored through photodetectors (D2, D3 and D1, respectively in Figure 2(A)) and a data acquisition system. Differential surface stress which is proportional to the cantilever deflection is then calculated by using Stoney's Formula with obtained spring constant and geometry of the cantilever.

After the exposure to alkanethiol, both the sensing and reference cantilevers are expected to be covered with alkanethiol SAM; therefore, reintroduction of alkanethiol vapors should not cause further differential bending of the cantilevers. In the last step, sensing and reference cantilevers were again exposed to alkanethiol vapors to ensure that measured surface stress change is associated with only alkanethiol formation.

## RESULTS AND DISCUSSION

Gold film on the cantilever was imaged using contact mode and grain size was determined to be 40 ± 10 nm (Figure 3). The mean square roughness of the gold surface was 2.07 ±0.23 nm for the 750 nm scan size. The stiffness of the cantilever were found to be in the range of 0.16-0.18 N/m resulting in a calculated thickness of approximately 1.7- 1.8 μm.

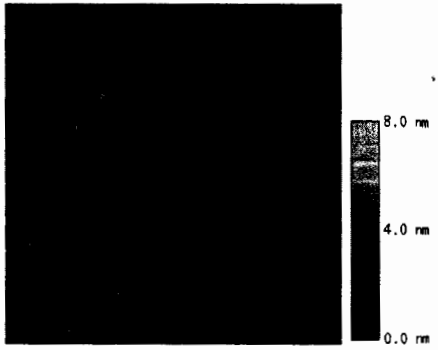


**Figure 3.** AFM image (750nm×750nm) of gold film microstructure on AFM cantilevers

Experimental measurements of surface stress induced due to vapor phase deposition of alkanethiol during a typical run are plotted in Figures 5(a), (b) and (c). Intensity of interfered beams monitored before introduction of alkanethiol vapor are plotted in Figure 5(a). Measured intensities are nearly constant and do not drift with time. The differential bending and the corresponding surface stress change during formation of alkanethiol SAMs on the sensing cantilever respect to reference cantilever are shown in Figure 5(B). As soon as alkanethiol solution is injected, the sensing cantilever undergoes tensile surface stress change first and subsequently, as expected compressive surface stress develops on the sensing cantilever.

According to Figure 5(B), alkanethiol SAMs rapidly form in the early stages, 10 minutes after injection, but it took about 50 minutes to complete SAM formation (final saturation). Surface condition of cantilevers such as cleanliness, roughness, and the condition of gold deposition on the cantilever's surface influence on the pattern as well as magnitude of surface stress change. In addition, the distance of cantilever to the location where alkanethiol droplets are introduced was 10 cm away. The second development of surface stress change in Figure 5(B) is due to slow arrival of alkanethiol molecules or slow saturation of closely packed SAM on sensing cantilever. As a result, final surface stress change was 0.28 ± 0.02N/m and the corresponding differential banding was 180 ± 10 nm at grain size of gold surface was 40 ± 10 nm.

After the SAM formation on the sensing cantilever, sensor was again exposed to alkanethiol vapors. Intensity of the interfered beams measured during second exposure of alkanethiol is plotted in Figure 5(c). As shown in the Figure 5 (c), variations of the interfered beam intensities were within the system's normal noise range. A minimal surface stress change during re-introduction of the alkanethiol vapors indicates that both sensing and reference cantilever are covered with alkanethiol SAM. Furthermore, it indicates surface stress change observed during the first introduction is unambiguously associated with SAM formation on sensing cantilever. Previous reports [4] have indicated that distance of cantilever to the location where alkanethiol droplets are introduced, condition of gold surface like cleanliness and roughness, and grain structure of the gold on the cantilever's surface affects the kinetics and magnitude of surface stress development. Among those conditions, the microstructure of gold film significantly influences the development of the surface stress during the formation of Alkanethiol SAMs [4].

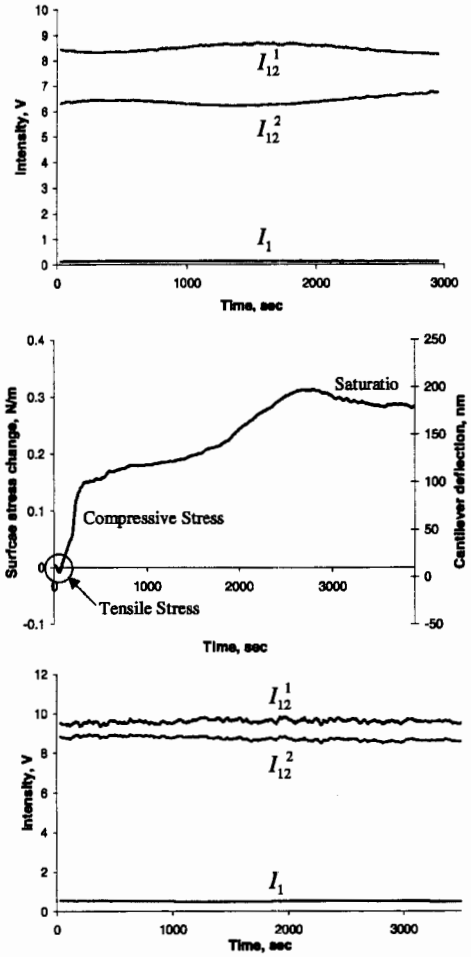


**Figure 5.** Surface stress change and the corresponding sensing cantilever deflection respect to reference cantilever (A) Intensity of interfered beams before deposition, (B) Differential surface stress during deposition; (C) Inensity of interfered beams due to alkanethiol exposure after deposition.

## CONCLUSIONS

A miniature sensor based on two microcantilevers – a sensing and reference pair – is developed for differential surface stress measurement and is explored for detection of chemical and biological species. High resolution interferometry is utilized to measure the differential surface stress developed due to absorption of chemical species on the sensing cantilever. Sensitivity of sensor measurement is not dependent on distance between the sensing surface and detector; as a result, surface stress sensor is amenable for miniaturization and array of sensors would be easily fabricated on a single MEMS device. Surface stress associated with alkanethiol formation on gold surface is measured to characterize the response of the sensor.

## ACKNOWLEDGMENTS

This work was supported by National Science Foundation Career Award and Seed Funding from Midwest Forensic Research Center

## REFERENCES

1. Thundat, T., R.J. Warmack, G.Y. Chen, and D.P. Allison, *Thermal and Ambient-Induced Deflections of Scanning Force Microscope Cantilevers.* Applied Physics Letters, 1994. **64**(21): p. 2894-2896.
2. Fritz, J., M.K. Baller, H.P. Lang, H. Rothuizen, P. Vettiger, E. Meyer, H.J. Guntherodt, C. Gerber, and J.K. Gimzewski, *Translating biomolecular recognition into nanomechanics.* Science, 2000. **288**(5464): p. 316-318.
3. Berger, R., E. Delamarche, H.P. Lang, C. Gerber, J.K. Gimzewski, E. Meyer, and H.J. Guntherodt, *Surface stress in the self-assembly of alkanethiols on gold.* Science, 1997. **276**(5321): p. 2021-2024.
4. Godin, M., P.J. Williams, V. Tabard-Cossa, O. Laroche, L.Y. Beaulieu, R.B. Lennox, and P. Grutter, *Surface stress, kinetics, and structure of alkanethiol self-assembled monolayers.* Langmuir, 2004. **20**(17): p. 7090-7096.
5. Raiteri, R., H.J. Butt, and M. Grattarola, *Changes in surface stress at the liquid/solid interface measured with a microcantilever.* Electrochimica Acta, 2000. **46**(2-3): p. 157-163.
6. Stevenson, K.A., A. Mehta, P. Sachenko, K.M. Hansen, and T. Thundat, *Nanomechanical effect of enzymatic manipulation of DNA on microcantilever surfaces.* Langmuir, 2002. **18**(23): p. 8732-8736.
7. Ulman, A., *An Introduction to Ultrathin Organic Films: From Langmuir--Blodgett to Self--Assembly* 1991, New York: Academic Press. 442.
8. Stoney, G.G., *The tension of metallic films deposited by electrolysis.* Proceedings of the Royal Society of London: A, 1909. **82**: p. 172-175.
9. Sader, J.E., J.W.M. Chon, and P. Mulvaney, *Calibration of rectangular atomic force microscope cantilevers.* Review of Scientific Instruments, 1999. **70**(10): p. 3967-3969.
10. Sader, J.E. and L. White, *Theoretical-Analysis of the Static Deflection of Plates for Atomic-Force Microscope Applications.* Journal of Applied Physics, 1993. **74**(1): p. 1-9.